

ANSWERS TO REVIEWERS

Iodine chemistry in the troposphere and its effect on ozone

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General Answer

We are grateful to the anonymous reviewer #1 and Dr. Rolf Sander for their very constructive suggestions and corrections. We have fully addressed point-by-point each of their comments, including updates on references and related works, clarifying descriptions of model inputs and configurations, estimations of the main processes controlling the iodine loading and rephrasing of misleading discussions and/or conclusions.

To facilitate the reading, the original comments made by the reviewers have been copy-pasted here using **bold font**, while our answers are given in regular font. Additionally, we have copied into this response letter the current changes made to the original manuscript, using a *blue* and/or *italic* font type.

1 Reviewer #1

1.1 General Answer

This paper reports a global modelling study of the abundance and impacts of iodine upon tropospheric chemistry and composition, based upon new insights into the sources of iodine species in the marine atmosphere, and current understanding of iodine oxide kinetics and photochemistry, effectively updating previous modelling studies from a couple of decades ago. The results show an important role for iodine chemistry in contributing to chemical ozone destruction in the troposphere, and a distinctive spatial distribution of atomic iodine in the mid-troposphere.

The manuscript makes an important integrative contribution to a topical area of atmospheric chemistry, providing quantitative assessments of iodine chemical impacts, while also communicating the uncertainty in iodine oxide photochemistry which limits more definitive assessments of its role. The use of two scenarios for IxOy photochemistry is appropriately conservative in this respect. There are a few areas where greater clarity is needed, and where further exploration of the uncertainties in the iodine source strength and photochemistry is warranted (outlined below); subject to revision addressing these comments, the paper is suitable for publication in ACP.

We thank the reviewer_#1 for his/her very useful comments and suggestions, which are addressed point-by-point below. We agree that further exploration of the uncertainties in the

1 iodine sources, chemistry and sinks is needed, and we expect that the changes introduced in
2 the main text help to emphasize which are the main areas where future studies should be
3 focused.

4 **1.2 General Points**

5 **1 The new HOI/I₂ iodine source to the MBL is a function of ozone deposition, amongst**
6 **other factors. Given that one finding of this work is a substantial role for iodine in**
7 **chemical ozone depletion, there must be some feedback at work with climate / radiative**
8 **forcing consequences. This aspect should be explored, at least qualitatively, in the**
9 **discussion and conclusions.**

10 We are glad that the reviewer has recognised the climatic importance of the coupling between
11 tropospheric ozone and iodine. Indeed, we have recently submitted a related work proposing a
12 climate feedback between the anthropogenically-driven increase in tropospheric ozone and
13 iodine emissions from the global oceans, which is currently under review in ACPD:

14 Prados-Roman, C., Cuevas, C. a., Fernandez, R. P., Kinnison, D. E., Lamarque, J.-F. and
15 Saiz-Lopez, a.: A negative feedback between anthropogenic ozone pollution and enhanced
16 ocean emissions of iodine, Atmos. Chem. Phys. Discuss., 14(15), 21917–21942,
17 doi:10.5194/acpd-14-21917-2014, 2014.

18 As we only had a draft version of the iodine-ozone feedback paper when we submitted the
19 original manuscript, no mention was made to this relevant and related work. Following the
20 reviewer's suggestion, we have included a qualitative discussion of the ozone-iodine
21 feedbacks and referred to Prados-Roman et al. (2014) for further details:

22 *...Within the MBL, and as a consequence of the increased inorganic iodine loading due to the*
23 *direct oceanic injection of reactive I₂/HOI species, IO_xLoss cycles represent the second most*
24 *important ozone depleting family (IO_xLoss^{MBL} ≈ 17% (27%) for Base (J_{IxOy}), respectively),*
25 *surpassing in efficiency the contribution of HO_xLoss. This additional source of inorganic*
26 *iodine depends on the deposition of ozone on the ocean's surface, and then acts as a natural*
27 *buffer for ozone pollution in the lower troposphere: e.g., the warming effect of anthropogenic*
28 *ozone in the global marine troposphere can be reduced by at least 3–10 % when inorganic*
29 *iodine sources are considered (see Prados-Roman et al. (2014) for details). The negative*
30 *geochemical feedback loop between anthropogenic ozone and oceanic inorganic iodine*
31 *emissions proposed by Prados-Roman et al. (2014) exemplifies ocean biogeochemical cycles*
32 *being affected by anthropogenic emissions....*

33

34 **2 The source strength values are critical to this study. How uncertain are these – it**
35 **would be useful to indicate the range of values from e.g. the various reviews, and for the**
36 **“new” I₂/HOI source, the confidence level in its magnitude...**

37 We acknowledge that there are uncertainties in the source strength values and agree that they
38 are critical to our analyses. Below we demonstrate that our fluxes are in line with other values
39 from the literature. For further details, please refer to Prados-Roman et al., ACPD, (2014).

40 Table 3 of Ordóñez et al., (2012) shows that the global annual fluxes of VSL halocarbons
41 estimated in that analysis and used in this manuscript are in good accord with those
42 previously shown in the literature. As recognised by other authors (e.g. Jones et al., GRL,
43 2010; Mahajan et al., ACP, 2010) an additional inorganic flux is needed to support the
44 observed IO concentrations. Initially this was accounted for in CAM-Chem by a global total

1 I₂ emission field of ~1200 Gg yr⁻¹ (Saiz-Lopez et al., 2012b). As indicated in that paper, their
2 resulting average I₂ flux over the tropical oceans (~4.9 × 10⁷ molec cm⁻² s⁻¹) is very close to
3 the constant day and night flux of ~5.0 × 10⁷ molec cm⁻² s⁻¹ considered by Mahajan et al.
4 (2010) for the tropical Atlantic. More recently Großmann et al. (ACP, 2013) calculated I₂
5 fluxes of a similar order of magnitude, but somewhat higher, for the Western Pacific (10–34 ×
6 10⁷ molec cm⁻² s⁻¹, see Table 3 of that paper). Carpenter et al. (Nature Geo, 2013) introduced
7 the parameterisation of HOI/I₂ fluxes used in this manuscript; their estimated fluxes of iodine
8 atoms (see their Figure 3a) are similar to those in Mahajan et al. (2010) and Saiz-Lopez et al.
9 (2012b).

10 The current implementation of inorganic iodine emissions in CESM represents an
11 improvement in the treatment of that process compared to Saiz-Lopez et al. (2012b). The
12 I₂/HOI source – based on Carpenter et al. (2013) and following Prados-Roman et al. (ACPD,
13 2014) – yields a global oceanic flux of ~1.9 Tg (I) yr⁻¹ and depends on the deposition of
14 tropospheric ozone to the ocean surface. This is somewhat higher than the ~1.2 Tg yr⁻¹ value
15 of Saiz-Lopez et al. (2012b), in line to the findings of Großmann et al. (ACP, 2013). To make
16 these points clear we have modified the text as follows:

17 *...The global modelled emissions of HOI/I₂ account for ~1.9 Tg (I) yr⁻¹ and depend on the*
18 *deposition of tropospheric ozone to the ocean surface, the sea surface temperature and the*
19 *wind speed (see Prados-Roman et al. (2014) for further details on the implementation of the*
20 *inorganic iodine source). This additional inorganic source is somewhat larger than the ~1.2*
21 *Tg (I) yr⁻¹ value of Saiz-Lopez et al. (2012b) and within the range of values required to*
22 *reconcile IO measurements in the MBL at coastal sites (i.e., in the range of (10 – 70) × 10⁷*
23 *atoms (I) cm⁻² s⁻¹; see Mahajan et al. (2010), Großmann et al. (2013) and references*
24 *therein)...*

25 **...The statement on p. 19999 that without CH₃I iodine would have a negligible impact**
26 **on the FT/UT seems to imply that the (very short lived) I₂/HOI source has no impact on**
27 **iodine abundance or effects outside the MBL – can this be clarified?**

28 With regards to the impact of the additional HOI/I₂ inorganic source in the FT and UT,
29 Figure 2 of the manuscript clearly shows that even when the HOI/I₂ flux is the largest source
30 of iodine at the surface, the direct source of atomic I from inorganic precursors (J_{IBr}+J_{ICl}) is
31 rapidly surpassed by the photodecompositions of VSL iodocarbons. Above approximately 5
32 km, CH₃I photolysis becomes the dominant source of I atoms in the atmosphere, and thus
33 controls the source of iodine in the upper troposphere.

34 Evidently, transport of inorganic I_y from the MBL to the FT and UT will also have an impact
35 on the total I_y loading in the upper troposphere. The strength of this contribution will largely
36 depend on the independent wet-removal of each species. A quantitative analysis of the
37 importance of each of the sources and sinks within the global troposphere requires running a
38 large set of sensitivities simulations, which cannot be afforded at this time, but will certainly
39 be considered in the future.

40 We appreciate the reviewer for highlighting this misleading implication in the original
41 manuscript, which has now been modified as follows:

42 *...It is worth noting that the photodecomposition of CH₃I is the first step providing iodine*
43 *atoms in the mid- to upper-troposphere, and without the contribution from this organic*
44 *precursor the inorganic iodine loading in the FT and UT would be significantly reduced.*
45 *Additionally, direct transportation of I_y species from the MBL, sustained by stoichiometric*
46 *heterogeneous recycling on sea-salt aerosol, increase the impact of iodine chemistry on the*

1 ozone budget as described in Sect. 3.5...

2

3 **3 The authors do a good job of inclusion of many recent lab studies in their IO_x reaction**
4 **scheme, but one reaction neglected appears to be IO + CH₃O₂, shown to have**
5 **potentially substantial impacts for IO and to be competitive with (e.g.) IO + HO₂ and IO**
6 **+ NO₂ (e.g. Dillon et al. PCCP 2006). Is this a conscious choice? What is the impact?**
7 **This reaction should be included in the relevant O₃ loss cycle (products dependent,**
8 **which will increase the range of O₃ reductions).**

9 In our previous iodine chemistry review paper (Saiz Lopez et al., 2012, section 4.2.1.2.4.) we
10 pointed out that there is some controversy about the rate constant: Dillon's value $k = (2 \pm 1) \times$
11 $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is a factor of ~30 lower than the results reported by Bale et
12 al. (2005) and Enami et al. (2006). We think Dillon et al. result is more reliable because (i)
13 their PLP-LIF set-up is less prone to interferences in complex reaction systems than the low
14 tube approach, and (ii) they evaluated more carefully potential interferences of secondary
15 radical chemistry. Dillon et al. argued that the chemical scheme used to study the reaction
16 would always suffer from CH₃O₂ losses and interfering reactions with CH₃O and HO₂
17 radicals that would generally lead to an overestimation of the rate coefficient.

18 Drougas and Kosmas (2007) performed calculations on this system at CCSD(T) level of
19 theory and concluded that the most likely product channels are:

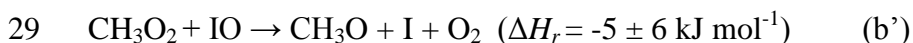


22 However, the theoretical study yields results inconsistent with the endothermicity of channel
23 (a), which we have re-evaluated using updated values of the heats of formation of the species
24 involved:

25

Species	$\Delta H_f(298 \text{ K})$	Uncert.	Reference
I	107.16	0.04	CODATA
IO	124.1	2.0	Exp. Dooley et al. (2008)
OIO	122.1	2.0	Exp. Gomez Martin & Plane (2009)
IOO	98	4	Calc. Peterson (2010)
CH ₃ O	21.0	2.1	Ruscic et al. (2005)
CH ₃ O ₂	9	5	Knyazev & Slagle (1998)

26 According to recent multi-reference *ab initio* calculations by Peterson (2001), IOO is bound
27 by just 9.5 kJ mol⁻¹ with respect to I + O₂, which would result in the following overall
28 process:



30 This analysis is consistent with the lower limit for the I atom yield of 0.4 reported by Bale et
31 al. and the upper limit for the OIO yield of 0.1 reported by Enami et al.

1 Dillon et al noted that considering IO and CH₃O₂ mixing ratios in the MBL of 5 and 30 pptv,
 2 respectively, the CH₃O₂ reaction would create a flux of OIO similar to that from the IO self-
 3 reaction. We have discarded the OIO-forming channel based on its endothermicity, and
 4 therefore a direct impact of CH₃O₂ + IO on I_xO_y formation can also be discarded.

5 Vogt et al. (1999), assumed $k(\text{CH}_3\text{O}_2 + \text{IO}) = 2.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and a unit
 6 branching ratio for I atom production (b') in their MBL modelling work, and found a
 7 significant effect on O₃ depletion rates due to I atom product. Dillon et al noted that the effect
 8 would be insignificant if their 10 times lower value for the rate constant was used. Due to the
 9 rapid oxidation of the methoxy radical (CH₃O + O₂ → CH₂O + HO₂), we have performed a
 10 sensitivity study including the following reaction and analysed its impact on ozone losses:



12 Our results confirm Dillon's conclusion: we find an increase of 0.5% in ozone depletion in the
 13 MBL and 0.1% integrated over the whole troposphere. Note that formation of HO₂ and
 14 formaldehyde leads ultimately to formation of ozone. We therefore conclude that with the
 15 current understanding on the CH₃O₂ + IO reaction, it can be considered as unimportant from
 16 the point of view of ozone loss. Moreover, the inclusion of this reaction in the chemical
 17 scheme results in negligible impacts on the partitioning of I_y species in the troposphere, with a
 18 maximum impact on individual species of 1.8% (for I in the J_{IxOy} scenario). Due to the large
 19 and expensive computing resources required to perform the full set of simulations (Base +
 20 J_{IxOy} schemes), we decided not include the reaction but will certainly include it in future
 21 studies for completeness.

22 The reaction has been added to Table 1 and the following text has been added to the footnote:



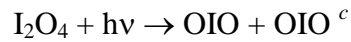
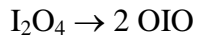
23 ^h Updated heats of formation for IO, OIO, and CH₃O₂ [Dooley et al, 2008; Gomez
 24 Martin and Plane, 2009; Knyazev & Slagle, 1998] show that the only accessible exothermic
 25 product channel of CH₃O₂ + IO [Drougas and Kosmas, 2007] is CH₂O + I + O₂ (ΔH_r = -5 ±
 26 6 kJ mol⁻¹), consistent with the high yield of I and low yield of OIO found experimentally
 27 [Bale et al., 2005; Enami et al., 2006]. Sensitivity studies have been carried out using the
 28 preferred rate constant for this reaction of 2 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ [Dillon et al., 2006],
 29 resulting in an enhancement of the ozone loss of 0.5% in the MBL and of less than 0.1%
 30 integrated throughout the troposphere in the J_{IxOy} scenario, and similarly negligible
 31 enhancements in the Base scenario. Impacts in the I_y partitioning are also very minor.

32

33 **4 p.19993/19994 it would be useful to give indicative values for the (pseudo) first order**
 34 **rate constants for IxOy loss through decomposition, uptake and photolysis to guide the**
 35 **account.**

36 We understand that the reviewer suggests giving absolute rate values (i.e., molec cm⁻³ s⁻¹) for
 37 the reactions that produce a net loss of IxOy (-d[IxOy]/dt)_{process} for each process. The related
 38 main processes are:

Thermal Decomposition (Table 1)	Photolysis (Table 2):
I ₂ O ₂ → OIO + I	I ₂ O ₂ + hv → I + OIO ^c
I ₂ O ₂ → IO + IO	I ₂ O ₃ + hv → IO + OIO ^c



1 which represent a change in the partitioning between I_y species, and not actual sinks nor
2 sources. Another way of looking at these processes is focusing on the production rate of
3 reactive iodine produced on these reactions, as they follow the relationship:

$$4 \quad (d[\text{IO}_x]/dt)_{\text{process}} = (-d[\text{I}_x\text{O}_y]/dt)_{\text{process}}$$

5 (note that the photolysis of OIO to $\text{I} + \text{O}_2$ is so efficient that the formation of OIO from I_xO_y is
6 computed as $\text{IO}_x = \text{I} + \text{IO}$, see Fig.4 caption in the manuscript).

7 Figure 4 of the original manuscript shows zonal distributions of $(d[\text{IO}_x]/dt)_{\text{process}}$ up to 9 km
8 for 3 distinctive sources: Thermal decomposition of I_xO_y , Photolysis of I_xO_y and Photolysis
9 of CH_3I . Thus, in section 3.2 where the role of I_xO_y (within their uncertainties) is introduced,
10 we have already given an estimate of the rate constants for 2 of the 3 processes highlighted by
11 the reviewer. To clarify the similitudes on using either the left or the right hand side
12 expressions for the production or loss processes for I_xO_y and IO_x , the following equivalence
13 has been added:

14 *... The comparative release of reactive iodine species due to CH_3I photolysis (defined as*
15 *$d[\text{I}]/dt$) and that arising from the thermal and photolytic breakdown of I_xO_y (defined as*
16 *$d[\text{IO}_x]/dt = -d[\text{I}_x\text{O}_y]/dt$) is shown in Figure 4. Note that in Fig. 4 the losses of higher oxides*
17 *are equivalent to the production of reactive iodine and do not represent a net sink of iodine in*
18 *the atmosphere, but a change in partitioning between different I_y species.*

19 The only process highlighted by the reviewer that was not analysed in the original manuscript
20 is the mean loss of I_xO_y due to the uptake by sea-salt aerosols and washout (Tables 3 and 4).
21 As these processes represent a net sink of iodine in the atmosphere, and not a change in the
22 partitioning between different I_y species, we find it confusing to introduce additional panels
23 for these processes in Figure 4. Instead, those processes should be compared to the net
24 sources of iodine to the atmosphere either by VSL photodecomposition or by HOI/ I_2 oceanic
25 sources. The used units for representing these processes in the manuscripts are atoms (I) cm^{-2}
26 sec^{-1} and/or Tg (I) yr^{-1} . Quantitative estimations of iodine sources have already been given in
27 section 2.2 (see also the answer to point 2 above). We have now computed average net losses
28 for uptake on aerosol and washout in the MBL and FT, and include their values within the
29 text as follows:

30 *...Indeed, the Henry's law constant for HOI (K_H^{HOI}) has been adjusted between a more (Base)*
31 *and less ($J_{\text{I}_x\text{O}_y}$) efficient value within the range of measurements and uncertainties reported in*
32 *the literature (Sander, 1999; see also Table 4). This results in a total washout rate within the*
33 *tropics in the range of $\sim 6-7 \times 10^7$ atoms (I) $\text{cm}^{-2} \text{s}^{-1}$. For the $J_{\text{I}_x\text{O}_y}$ scheme, $\sim 95\%$ of the wet-*
34 *removal occurs in the MBL and FT and is controlled by the uptake on liquid droplets of HOI,*
35 *IONO_2 and I_xO_y (42%, 21% and 16% respectively). The Base scheme presents a*
36 *comparatively larger contribution from I_xO_y scavenging (30% compared to 12% for IONO_2)*
37 *due to the higher oxides accumulation, Note that from the overall I_xO_y sinks, only 15% occurs*
38 *due to irreversible deposition on sea-salt aerosols. Within the $J_{\text{I}_x\text{O}_y}$ scheme, the IONO_2*
39 *abundance increases significantly above 10 km, representing the most abundant nighttime*
40 *inorganic reservoir in the TTL ($\text{IONO}_2^{15\text{km}} = 0.4 \text{ pptv}$) and the main sink of iodine at these*
41 *heights.*

42

43 **5 p.20004 A further possibility (besides (i) and (ii) mentioned) would be that I_xO_y do**
44 **accumulate in the FT/UT. How do we know that this is not the case – are their e.g.**

1 **aerosol composition data / iodate loadings which can be cited ?**

2 We thank the reviewer for highlighting the original misleading implication of the 2 bullet-
3 points: the I_xO_y accumulation is evidently a possible scenario (although, at least for the
4 authors, improbable; and to our knowledge, never measured nor assumed in any study), and
5 we have stated so clearly at several points in the manuscript. But we agree that in the sentence
6 highlighted by the reviewer, the two bullet-points (i and ii) should be updated with the three
7 (i, ii and iii) possible scenarios:

8 *...Then, the modeling experiment performed here indicates that either: i) an unrecognized*
9 *removal processes for I_xO_y must exist in the FT and UT, ii) a substantial accumulation of*
10 *unreactive I_xO_y prevails in the upper troposphere or iii) a decomposition pathway releasing*
11 *active iodine, such as the photodecomposition proposed in the $J_{I_xO_y}$ scheme, occurs. As to the*
12 *authors knowledge there are no evidence for i) nor ii), we then suggest, based on*
13 *experimental and theoretical studies (i.e. Gómez Martín et al., 2005; Saiz-Lopez et al., 2008)*
14 *that the photochemistry of I_xO_y should be further investigated in order to reduce uncertainties*
15 *on the important chemical impacts of iodine chemistry.*

16

17 **6 The paper should reference Davis et al., JGR 101, 2135, 1996 as appropriate.**

18 We thank the reviewer for highlighting this omission. The reference has now been added.

19 Davis. D., J. Crawford, S. Liu, S. McKeen, A. Bandy, D. Thornton, F. Rowland and D. Blake,
20 Potential Impact of Iodine on Tropospheric Levels of Ozone and Other Critical Oxidants J.
21 Geophys. Res., 101, p 2135, 1996.

22

23 **7 Higher iodine oxides are assumed to undergo rapid uptake to sea salt aerosol leading**
24 **to a net sink. Is there evidence for this assumption? (p.19992)**

25 In the supplement of Ordóñez et al. (2012) we describe the assumed uncertainties and
26 approximations of sea-salt uptake followed by a net reaction. The same analysis can be
27 applied to the uptake (followed by removal) of I_xO_y species:

28 *“The processing of aqueous HOX to Br₂, BrCl, IBr, ICl and Cl₂ via reaction with Br-, Cl-*
29 *and I- takes only between 10 and 15 min on fresh sea-salt aerosols (McFiggans et al., 2000).*
30 *Since di-halogen molecules are insoluble they are rapidly released to the gas phase. As a*
31 *consequence, uptake of inorganic bromine and iodine species onto aerosols is the rate-*
32 *limiting step of the process (McFiggans et al., 2000) ... In CAM-Chem we do not explicitly*
33 *treat the aqueous phase chemistry in the bulk of the sea salt aerosols. Instead, we assume that*
34 *the limiting step for halogen recycling on sea salt aerosols is the first order rate of uptake*
35 *computed for a number of gaseous species using the free molecular transfer regime*
36 *approximation ...”*

37 Now we are applying the same methodology for the net uptake (i.e. without any further
38 halogen release) of I_xO_y species and use the same gamma values as those for $IONO_2$ (as you
39 indicate below). Regardless of the approximations of the parameterization, if there is not any
40 known formulation for gamma, the value used for gamma will probably dominate the
41 uncertainties in the implementation of this process. To the authors knowledge there are not
42 measurements of direct deposition and removal of I_xO_y into sea-salt aerosols. Then, we
43 cannot do much more in the absence of laboratory studies, which provide more detailed
44 formulations of that assumed rapid uptake.

1 As there are neither measurements nor estimates on the efficiency of this type of deposition,
2 we impose a gamma value identical to the one for IONO₂ (the iodine-containing species that
3 is recycled in sea-salt aerosols with the largest molecular weight, closer to those for I_xO_y). In
4 this way we were capable to maintain an equivalent total I_y loading in the troposphere for the
5 *Base* and *J*I_xO_y schemes. If this process is not considered, then the accumulation of I_xO_y in
6 the *Base* scheme produces a total I_y^{Base} >> I_y^JI_xO_y. It is worth noting that the net loss of
7 inorganic iodine due to sea-salt uptake is a minor contribution compared to the wet removal
8 of HOI and I_xO_y (see Henry constants for each species in Table 4 and quantitative answer to
9 point 4 above). Indeed, deposition of I_xO_y in sea-salt represents less than 15% of the wet
10 removal of I_xO_y in liquid clouds.

11 *...The non-reactive uptake of the higher iodine oxides is also proposed to proceed efficiently*
12 *on sea-salt aerosols following the free regime approximation, although this additional sink of*
13 *atmospheric iodine is a minor contributor compared to scavenging of I_xO_y in water clouds...*

14 *... Note that from the overall I_xO_y sinks, only ~15% occurs due to irreversible deposition on*
15 *sea-salt aerosols.*

16

17 **8 I₂O₄ spectrum – is there a need for allowance for solution shifts in the spectrum cf.**
18 **gas phase? The quantum yields / photolysis thresholds are not mentioned for**
19 **I₂O₂/I₂O₃/I₂O₄.**

20 The photolysis thresholds of the iodine oxides are mostly in the near infrared region:

21

	BE /kJ mol ⁻¹	Photolysis threshold /nm
I ₂ O ₂ → I + OIO	53	2267
I ₂ O ₂ → IO + IO	68	1759
I ₂ O ₃ → IO + OIO	165	725
I ₂ O ₃ → IO ₃ + I	188	637
I ₂ O ₄ → OIO + OIO	100	1196
I ₂ O ₄ → IO + IO ₃	138	867

22

23 Bond energies are taken from Galvez et al. (2013). There is very limited information about
24 the photochemistry of I_xO_y and in particular no studies have been conducted on their
25 photolysis quantum yields and products. As shown in the table above, different product
26 channels are accessible for each I₂O_y species. For simplicity, our approach has been to
27 consider a single photolysis channel with unit quantum yield for each species, via break-up of
28 the weakest bond, but the large uncertainties in these assumptions are acknowledged
29 throughout the text.

30 The following sentence has been added to the text (p. 19992, l. 23):

31 *...Prominent featureless absorption bands of I_xO_y species have been experimentally observed*
32 *in the UV region (Bloss et al., 2001; Gómez Martín et al., 2005; Spietz et al., 2005). The*
33 *photolysis thresholds of the iodine oxides are mostly in the near infrared region (Gálvez et*
34 *al., 2013). Therefore, it is plausible that in the atmosphere photochemical decomposition of*
35 *I_xO_y back to IO_x will compete with thermal decomposition and uptake by aerosol, reducing*
36 *the atmospheric losses by washout and/or scavenging.*

37 Regarding the shifting of the I₂O₄ spectrum, it is certainly possible that its gas phase spectrum

1 is blue-shifted compared to the spectrum in solution, which would result in lower photolysis
2 rates for this species. We have carried out ab initio calculations using the time-dependent
3 DFT method which suggest that the spectrum of the solvated I₂O₄ molecule is shifted to the
4 blue. However, these calculations are rather qualitative and given the large number of
5 uncertainties involved in the photochemistry of the I_xO_y we prefer to use the spectrum in
6 solution without any guessed or estimated wavelength shift. In p. 19997, l 14-21, we
7 specifically state that ‘*many uncertainties still exist on which are the dominant photochemical*
8 *processes affecting I_xO_y species*’ and that the rationale of our modelling work is presenting
9 ‘*our best estimate of the **upper and lower range** of tropospheric iodine loading and its*
10 *partitioning for the Base and J_{IxOy} schemes*’.

11 The following sentence has been added (p. 19993, l. 12):

12 *...Note that the gas phase absorption spectrum of I₂O₄ is likely to be blue-shifted with respect*
13 *to its spectrum in solution and therefore this may result in overestimation of the atmospheric*
14 *photolysis rates.*

15

16 **1.3 Minor Comments**

17 **p.19988 L17+ needs rewording**

18 *Based on iodine’s faster catalytic ozone-depletion kinetics compared to that of bromine and*
19 *chlorine, box- and one-dimensional (Solomon et al., 1994; Davis et al., 1996; Vogt et al.,*
20 *1999; Calvert and Lindberg, 2004; Saiz-Lopez et al., 2007; Sommariva and von Glasow,*
21 *2012; Sommariva et al., 2012), and global (Saiz-Lopez et al., 2012b) modeling studies have*
22 *suggested the potential important role of iodine in the destruction of tropospheric ozone.*

23 **p.19996 L15 “of” not “on”**

24 Done.

25 **p.19999 L16 I don’t think “notorious” is the right term**

26 We replaced notorious by *evident*.

27 **p.20001 define WP**

28 WP has been defined as Western Pacific warm pool, and its regional area is shown by a black
29 rectangle in Fig. 6. In the original manuscript, we did not want to overload the reader with
30 several definitions and acronyms, and include it only on the caption of Figure 6. But
31 following the reviewer’s suggestions we have added the following sentence at the beginning
32 of section 3: Results and discussions:

33 *...Besides the standard 24 hour averaged streaming, time dependent output for day and night*
34 *has been generated considering the noon (11:30–12:30) and midnight (23:30–00:30) local*
35 *time, respectively, for all latitudes and longitudes. Additionally, the Western Pacific (WP)*
36 *warm pool area was defined by the equator (0°) and the 20° N parallels, and the 120°E and*
37 *165°E meridians (see black rectangle in Fig. 7).*

38 **p.20002 L12 some text missing after “during periods”**

39 *...The ratio maximizes during periods and within regions of strong convection, when poor-*
40 *ozone air-masses are rapidly transported from the lower troposphere to the lower TTL...*

41 **p.20006 L28 “dawn & dusk” preferable to “twilight” which implies evening only**

1 Done.

2 **p.20009 could usefully reference Solomon & Garcia JGR 1994 partitioning concept for**
3 **Cl / Br efficiency at ozone depletion**

4 *The differences between IO_{xLoss} and $BrOx-ClO_{xLoss}$ contributions can be explained based on*
5 *the higher reactivity and therefore shorter lifetimes of iodine species: i) due to the*
6 *comparatively longer lifetimes of organic bromo- and chloro-carbons, inorganic bromine and*
7 *chlorine cycles represent a major ozone loss process in the lower and middle stratosphere*
8 *(Solomon et al., 1994; Salawitch et al., 2005); and ii) the very fast catalytic reactions of*
9 *iodine species make IO_x ozone loss cycles to be up to 10 times faster than $BrOx-ClO_x$ cycles*
10 *for an identical I_y and Br_y basis (i.e. $IO_{xLoss}/I_y \approx 10 \times ClO_x-BrO_{xLoss}/Br_y$). The total I_y*
11 *abundance at the height where the relative IO_{xLoss} maximizes (~12 km) is in the range*
12 *(0.66–0.81) pptv for the (Base- J_{IxOy}) schemes, while for bromine, $Br_y^{12km} \approx 1.0$ pptv and*
13 *$Br_y^{17km} \approx 3.0$ pptv (Fernandez et al., 2014), indicating that even when Br_y abundances are*
14 *larger in the upper troposphere, the greater O_3 destruction efficiency of IO_x makes iodine the*
15 *dominant halogen contributing to tropospheric ozone loss, throughout the tropics and mid-*
16 *latitudes (see Table 6).*

17 **p.20010 line 6/7 phrasing needs attention**

18 *...The vertical distribution of tropospheric ozone loss due to halogen chemistry within the*
19 *tropics is very similar for both schemes considered here (25% for the MBL, 65 % for the FT*
20 *and 10 % for the UT). This indicates that most of the ozone loss due to iodine occurs in the*
21 *free troposphere in agreement with previous estimates (Saiz-Lopez et al., 2012b)...*

22

23 **p.20024 table caption is not accurate for $IxOy$ – needs to reflect account in text.**

24 *...Photolysis rates are computed online considering the actinic flux calculation in CAM-*
25 *Chem. The absorption cross-sections and quantum yields for all species besides the I_xO_y have*
26 *been taken from IUPAC-2008 (Atkinson et al., 2007, 2008) and JPL-2010 (Sander et al.,*
27 *2011).*

28 ^a *radical organic products are not considered.*

29 ^b *only the reaction channel reported in JPL 06-02 (Sander et al., 2006) is considered.*

30 ^c *photolysis reactions only considered in the J_{IxOy} scheme. The absorption cross-sections*
31 *reported in Sect. 2.2 (see Fig.1) have been used...*

32

33

1 *****

2 **2 Reviewer #2 RS**

3 *****

4 **2.1 General Answer**

5 **Saiz-Lopez et al. investigate the global effect of tropospheric iodine chemistry. The study**
6 **is very interesting and I recommend publication in ACP after considering some**
7 **suggestions as described below.**

8 We thank Dr. Rolf Sander for his positive and constructive feedback.

9 **My only major criticism is that the manuscript is based on a model version which has**
10 **not been described in detail in the literature yet. For the chemical mechanism, 5**
11 **different papers are cited (Emmons et al., 2010, Kinnison et al., 2007, Wegner et al.,**
12 **2013, Ordóñez et al., 2012, Fernandez et al., 2014). To fully understand the chemistry**
13 **calculations, the reader has to combine the reactions from these publications and add**
14 **the new iodine reactions as well...**

15 **...To add a full model description into this manuscript would probably increase the size**
16 **of the paper too much. In my opinion, the best solution would be to provide a full model**
17 **description in a specialized journal (e.g., Geoscientific Model Development) and then**
18 **describe only the different sensitivity studies (base, JI_xO_y , . . .) in this manuscript...**

19 We understand the reviewer's concern about the number of related papers in which the
20 implementation of halogen chemistry in CAM-Chem and CESM is based. As he stated,
21 including a complete and detailed description of the model would imply pointing to a
22 different and specialized journal and/or a Technical Report. However we think it is not the
23 time to do that yet. The extension of halogen chemistry in CAM-Chem – including the
24 photochemical breakdown of VSL sources of bromine and iodine as well as other related
25 processes – was documented only two years ago by Ordóñez et al. (2012). That paper is still
26 the base for the most recent updates/implementations such as those documented in Fernandez
27 et al. (2014) and here. The extension of halogen chemistry in CESM is still ongoing and the
28 aim of the present manuscript is not to provide a full description of all halogen processes in
29 the model. Therefore, we believe it is not convenient to further extend the length of the
30 current manuscript, but to focus here on the relevant scientific implications of iodine
31 chemistry in the troposphere. We appreciate Rolf Sander's constructive comment and his
32 suggestion will be considered in the future once the halogen model configuration reaches an
33 operational final status.

34 Even when the details on how the main processes considered have been included in the model
35 are cited in previous published papers, all the chemical equations and source/deposition
36 processes for iodine have been included in Tables 1-4. Thus, any research group willing to
37 include in their model an equivalent chemical mechanism to the one used in this work
38 (including the *Base* and JI_xO_y schemes), should only need to refer to this manuscript.
39 Evidently, for reactions of other halogen species (bromine and chlorine) and/or organic
40 compounds not related to iodine chemistry, further references would have to be considered.

2.2 A couple of further points regarding the model are also unclear to me:

As mentioned above, all the iodine-related processes are detailed in this manuscript and we think it is beyond the scope of this paper to provide with a full description about the model implementation of each process. However, we present here a brief and general response to each of the Reviewer concerns, pointing out the corresponding reference and indicating the respective changes introduced in the manuscript, if applicable:

• Page 19990, lines 21-23: “VSL oceanic sources of CH₂I₂, CH₂ICl and CH₂I₂Br are based on parameterizations of chlorophyll a satellite maps” How do these parameterizations work? Can you provide the data files that were used?

The development of the VSL oceanic emissions inventory used in this study has already been described in detail (Ordóñez et al., 2012). The approach used was parameterized as follows:

$$E = 1.127 \times 10^5 \times f \times r \times \text{chl-a}$$

where E is the emission flux for each VSL halocarbon species, f is a species and ocean dependent factor that was adjusted iteratively, following a top-down approach, to match background observations of the atmospheric mixing ratios of those species; r is a coast-to-ocean enhancement factor and chl-a are satellite maps gridded data from SeaWiifs. We believe it is not necessary to repeat all of this information clearly presented in Ordóñez et al. (2012) and refer the reader to that paper in the revised version of this manuscript.

...VSL oceanic sources of CH₂I₂, CH₂ICl and CH₂I₂Br are based on parameterizations of chlorophyll-a satellite maps, including latitudinal variations between 50°N–50°S, a time dependent ice-mask for polar oceans and an annual seasonality (see Ordóñez et al. (2012) for details)...

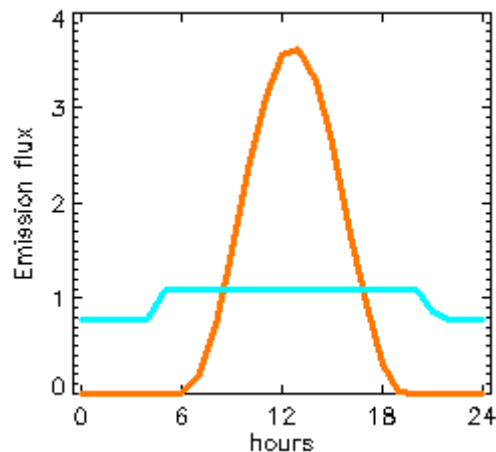
The VSL oceanic emissions files used in this study are available for use upon request. Indeed, the Ordóñez et al. (2012) inventory participated in a concerted evaluation of different emissions inventories of VSL bromocarbons (Hossaini et al., 2013).

Hossaini, R., Mantle, H., Chipperfield, M. P., Montzka, S. A., Hamer, P., Ziska, F., Quack, B., Krüger, K., Tegtmeier, S., Atlas, E., Sala, S., Engel, A., Bönisch, H., Keber, T., Oram, D., Mills, G., Ordóñez, C., Saiz-Lopez, A., Warwick, N., Liang, Q., Feng, W., Moore, F., Miller, B. R., Marécal, V., Richards, N. A. D., Dorf, M., and Pfeilsticker, K.: Evaluating global emission inventories of biogenic bromocarbons, Atmos. Chem. Phys., 13, 11819–11838, doi:10.5194/acp-13-11819-2013, 2013.

• Page 19991, lines 1-2: “For the emissions of most VSL iodocarbons we follow a solar diurnal profile” What function is used for the diurnal profile? A sine function, a bell shape, or something else?

For most of the VSL bromo- and iodo- carbon species we use a diurnal profile based on the photochemical active incoming radiation on each oceanic grid-box, although different partitioning between daytime and nighttime contributions was considered. The function shape for most cases is leptokurtic, i.e. more peaked than a “well bell-shaped” function. The oceanic sources depend on the geographical location (latitude), time of the day and time of the year, with emissions peaking in the early afternoon and zero at night as well as higher emissions in summer than in winter (the emissions have even been set to zero for high-latitudes in winter). The orange curve in the Figure below shows a typical diurnal profile for most halocarbons

1 at midlatitudes, while the blue line represents the profile imposed to CH₂I₂ emissions, with
2 no-null emissions at night. See Ordóñez et al. (2012) for details.



3
4 ...For the emissions of most VSL iodocarbons we follow a solar diurnal profile, with
5 emissions peak in the early afternoon and null emissions at night. The exception is CH₂I₂
6 which showed an improved agreement with measurements when ~1/4 of the total emissions
7 occurs during the night (Ordóñez et al., 2012)...

8
9 • Page 19991, lines 7-8: Emissions are given in Tg/yr. I assume that the emissions are
10 injected into the lowest model layer. Thus, the concentration change critically depends
11 on the height of this layer. What is the height of the lowest model layer?

12 This is a good point. Yes indeed, the oceanic emissions (both inorganic and VSL halocarbons)
13 are released only into the lowest model layer. Its altitude, defined as the distance between the
14 ocean surface and the interface between the 1st and 2nd lowest levels is approximately 120-150
15 m. The text has been updated accordingly.

16 ...In addition, inorganic iodine oceanic sources have been included in the *lowest layer of the*
17 *model (~150 m height over the oceans)*, based on recent laboratory studies that determined
18 the abiotic gaseous emission of HOI and I₂ following the oxidation of aqueous iodide by
19 atmospheric ozone *on the ocean surface* (Carpenter et al., 2013; MacDonald et al., 2014)...

20
21 • Page 19991, lines 8-9: “The global modelled emissions [. . .] depend on the deposition
22 of tropospheric ozone to the ocean surface, the sea surface temperature and the wind
23 speed.” What functions were chosen to describe these dependencies?

24 The exact formulations of the abiotic HOI/I₂ sources included in the model have been
25 described in another paper from our group (Prados-Roman et al., 2014). We did not cite this
26 related work in the original manuscript because we only had a draft version, which is now
27 under review in ACPD. We have now included its citation. Please see also the 1st answer to
28 reviewer #1.

29 ...The global modelled emissions of HOI/I₂ account for ~1.9 Tg (I) yr⁻¹ and depend on the
30 deposition of tropospheric ozone to the ocean surface, the sea surface temperature and the
31 wind speed (see Prados-Roman et al. (2014) for further details on the implementation of the
32 inorganic iodine source)...

1 The formulation introduced by Prados-Roman et al. (2014) is shown below:

2 *This emission function was included in CAM-Chem following the parameterization derived by*
3 *Carpenter et al. (2013):*

$$4 \quad \text{ISG} = \text{Flux}(\text{HOI}) + 2 \times \text{Flux}(\text{I}_2), \quad (1)$$

5 *where*

$$6 \quad \text{Flux}(\text{HOI}) = [\text{O}_3] \times \left(4.15 \times 10^5 \times \left(\frac{\sqrt{[\text{I}_{\text{aq}}^-]}}{w} \right) - \left(\frac{20.6}{w} \right) - 23600 \times \sqrt{[\text{I}_{\text{aq}}^-]} \right) \quad (2)$$

$$7 \quad \text{Flux}(\text{I}_2) = [\text{O}_3] \times [\text{I}_{\text{aq}}^-]^{1.3} \times \left(1.74 \times 10^9 - \left(6.54 \times 10^8 \times \ln w \right) \right), \quad (3)$$

8 *being w the wind speed (m s^{-1}), $[\text{O}_3]$ the surface ozone mixing ratio (nmol mol^{-1}) and $[\text{I}_{\text{aq}}^-]$*
9 *the concentration of aqueous iodide (mol dm^{-3}) (Carpenter et al., 2013). Based on the work of*
10 *MacDonald et al. (2014), the sea surface temperature (SST, K) was used as a proxy for*
11 *describing $[\text{I}_{\text{aq}}^-]$:*

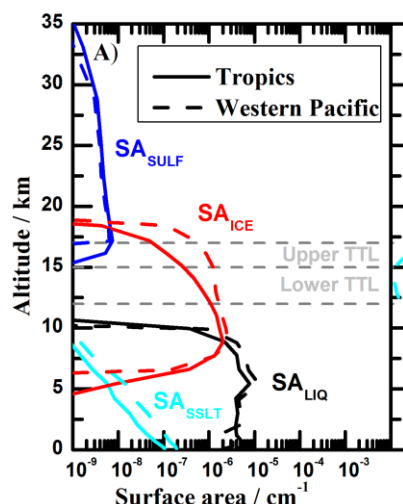
$$12 \quad [\text{I}_{\text{aq}}^-] = 1.46 \times 10^6 \times \exp\left(\frac{-9134}{\text{SST}}\right). \quad (4)$$

13

14 • **Page 19992, line 7: “Sea-salt heterogeneous recycling reactions for HOI, IONO and**
15 **IONO2 are also included in the chemical mechanism”** These reactions depend on the
16 **available aerosol surface. Can you describe (or plot) the model-calculated sea-salt**
17 **aerosol distribution?**

18 • **Page 19992, line 18: “scavenging in water and ice clouds”** These reactions depend on
19 **the availability of clouds. Can you describe (or plot) the model-calculated cloud**
20 **distribution?**

21 We thank the reviewer for highlighting this important point, which was unintentionally
22 omitted from the original manuscript because it was given in a tightly related paper recently
23 accepted for publication in ACP (Fernandez et al., 2014). There, in Figure 10a, we present
24 vertical profiles of the Surface Area (SA) for sea-salt (SA_{SSLT}), water-clouds (SA_{LIQ}), ice-
25 crystals (SA_{ICE}) and Stratospheric Sulfate (SA_{SULF} , not relevant for this paper). The CAM-
26 Chem configurations used in that paper and in the present manuscript are identical, so the
27 presented values for the tropical annual average (full lines) and the tropical Western Pacific
28 (dashed lines) are also valid here.



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We have updated the manuscript as follows:

...The vertical variation of the surface area density (SA) of liquid droplets (SA_{LIQ}) and sea-salt aerosols (SA_{SSLT}) used to compute the heterogeneous recycling reactions and the wet removal of inorganic iodine, respectively, is described and shown in Fig. 10a of Fernandez et al. (2014).

9 • I noticed that the reaction **OIO + OH (Plane et al, 2006) is not included. Is it not**
10 **important?**

11 Plane et al. (2006) attempted unsuccessfully to study of this reaction experimentally.
12 Although they observed OH removal, they attributed it to an excess of I₂ formed from the
13 CF₃I/N₂O/hv scheme ($k(I_2 + OH) = 2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Since the OIO concentration
14 was observed to be generally lower than the concentration of I₂ by one order of magnitude, a
15 similar rate constant for OIO + OH would have resulted in a small contribution of this
16 reaction to the observed removal rate. Thus, Plane et al. used statistical rate theory
17 calculations to estimate the rate constant, using molecular parameters from ab initio
18 calculations. They found that formation of HOIO₂ could occur by the simple addition of OH
19 to OIO, promoted by the substantial long-range attraction between the large dipole moments
20 of OH and OIO. Moreover, the reaction would be in its high pressure limit above 20 Torr,
21 implying a rate constant at room temperature close to the dipole-dipole rate constant. The
22 approach of Plane et al. is sound and the uncertainty in the rate constant of ~20% seems
23 realistic.

24 Very little is known about the gas phase properties of HOIO₂ (iodic acid), apart from the bond
25 energy calculated by Plane et al. of ~204 kJ mol⁻¹. We have carried out ab initio calculations
26 using time-dependent DFT and found that the absorption spectrum of HOIO₂ could
27 significantly blue shifted with respect to those of the I_xO_y, which would make it more
28 photostable. On the other hand, iodic acid is very soluble in water and should be lost to
29 aerosol efficiently, although uptake coefficients are, as for the I_xO_y, not available.

30 In the MBL ([IO]~0.5 pptv, [OH]~0.05 pptv), the first order loss rate of OIO from OIO + OH
31 ($k \sim 5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) should be smaller but of the same order than from IO + OIO
32 ($k \sim 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This should create a flux of HOIO₂ in the MBL smaller but

1 comparable to the flux of I_2O_3 , and similar to the I_2O_4 flux. The thermal and photo-stability of
2 HIO_3 should lead to its accumulation in the atmosphere in a similar manner to the
3 accumulation of I_xO_y in the *Base* scenario.

4 In summary, this reaction is potentially important and may provide a route for iodate
5 accumulation in aerosol via $HOIO_2$ uptake. However the level of uncertainty involving this
6 species, chiefly the lack of any experimental data has led us to exclude it from the
7 mechanism, given the large amount of tests that would be required to constrain its effects
8 properly. This however does not affect the main conclusions of the paper: if this reaction was
9 important and considered a sink for iodine, the situation would be more in line with *Base*
10 scenario, with less active iodine being recycled. Future experimental and modelling efforts to
11 measure the $OIO + OH$ reaction and observe its products would be very welcomed.

12 The reaction has been added to Table 1 with the following footnote:

13 *Fast rate constants and a thermally stable product $HOIO_2$ have been predicted theoretically*
14 *[Plane et al., 2006], but no experimental studies reporting observation of $HOIO_2$ and its*
15 *photochemical properties in the gas phase are available. Since the level of uncertainty is even*
16 *larger than for the I_xO_y , it has not been included in the mechanism.*

17

18 • **CAM-Chem, on which the current study is based, is a community model. Is the new**
19 **iodine code also available to the research community?...**

20 The implementation of a full tropospheric-and-stratospheric halogen scheme (both for
21 bromine and iodine) in CAM-Chem is currently under development. It has not been fully
22 validated for all geographical regions or altitude intervals. As the release of a community-
23 based code requires the completion of several validation routines, this extended halogen code
24 has not yet been included into the main CESM framework, but it will certainly be available
25 once the final version of the code is ready.

26

27 **2.3 Minor Comments**

28 • **According to the IUPAC Recommendations (page 1387 of Schwartz & Warneck “Units**
29 **for use in atmospheric chemistry”, Pure & Appl. Chem., 67(8/9), 1377-1406, 1995,**
30 **<http://www.iupac.org/publications/pac/67/8/1377/pdf>) the usage of “ppbv” and “pptv” is**
31 **discouraged for several reasons. Instead, “nmol/mol” and “pmol/mol” should be used**
32 **for gas-phase mole fractions. I suggest to replace the obsolete units.**

33 We thank Dr. Sander for his contribution to the unification of units as suggested by IUPAC
34 recommendations. However, we believe that the scientific atmospheric community is totally
35 familiar with the gas-phase mixing ratios units we have used in this work. As the iodine
36 manuscript presented here is tightly related to an accompanying paper on bromine already
37 accepted for publication in ACP (Fernandez et al., 2014), which also used ppbv and pptv
38 units, we find it counter-productive to change the units at this time.

39 However, we will consider the reviewer’s suggestions for future publications, and have
40 clarified the vmr units equivalency as follows:

41 *...Gas-phase mole fractions for all species are given in ppbv or pptv, which are equivalent to*
42 *the IUPAC recommended units nmol/mol and pmol/mol, respectively (Schwartz and Warneck,*
43 *1995)...*

1

2 • **Abstract, lines 17-20: “IO_xLoss cycles, without and with I_xO_y photolysis, represent**
3 **approximately (17-27) %, (8-14) % and (11-27) % of the tropical annual ozone loss for**
4 **the marine boundary layer (MBL), free troposphere (FT) and upper troposphere (UT),**
5 **respectively.”**

6 **I find this sentence very confusing and hard to read. It tries to describe a 2x3 matrix of**
7 **two model runs and three altitude ranges. I think for the abstract, it would be sufficient**
8 **to present only the upper limits, i.e., the results of the runs with I_xO_y photolysis.**

9 We thank Dr. Sander for highlighting this confusing sentence. We have removed the use of
10 the 3x2 matrix, but as the whole paper presents lower and upper limits, we believe that at least
11 an estimate of the lower impact limit must also be given in the abstract:

12 *...We calculate that the integrated contribution of catalytic iodine reactions to the total rate*
13 *of tropospheric ozone loss (IO_xLoss) is 2–5 times larger than the combined bromine and*
14 *chlorine cycles. When I_xO_y photolysis is included, IO_xLoss represent an upper limit of*
15 *approximately 27, 14 and 27 % of the tropical annual ozone loss for the marine boundary*
16 *layer (MBL), free troposphere (FT) and upper troposphere (UT), respectively; while the*
17 *lower limit throughout the tropical troposphere is ~9 %...*

18

19 • **Page 19988, lines 15-17: “Photochemical [. . .] and global modeling studies” Please**
20 **rephrase. Global models are also photochemical. Maybe you want to refer to “box and**
21 **global model studies”?**

22 The aim of the referred sentence was to highlight the fact that not all of the previous
23 modelling studies were performed using 3D Chemistry-Climate global models. As there is no
24 intention to give a historical nor methodological sequence of iodine studies as in a review
25 paper, we have modified the sentence as follows:

26 *Based on iodine’s faster catalytic ozone-depletion kinetics compared to that of bromine and*
27 *chlorine, box- and one-dimensional (Solomon et al., 1994; Davis et al., 1996; Vogt et al.,*
28 *1999; Calvert and Lindberg, 2004; Saiz-Lopez et al., 2007; Sommariva and von Glasow,*
29 *2012; Sommariva et al., 2012), and global (Saiz-Lopez et al., 2012b) modeling studies have*
30 *suggested the potential important role of iodine in the destruction of tropospheric ozone.*

31

32 • **Page 19992, line 20: Change “Absorption x-sections” to “Absorption cross sections”.**

33 Done.

34

35 • **Page 19996, line 11: “CH₂ICl is the di-halogen iodocarbon with the longest lifetime”**
36 **This is probably true for the species that are included in the model but are you sure that**
37 **the lifetime is also longer than that of CH₂FI?**

38 We have modified the sentence as follows:

39 *...Note that from all the VSL species represented in the model CH₂ICl is the di-halogen*
40 *iodocarbon with the longest lifetime (~8 hours) and it represents the strongest oceanic VSL*
41 *source on an iodine-atom basis...*

42

1 • Page 20006, lines 28-29: You attribute the top-hat shape to the reduced
2 photodissociation of IO radicals during sunrise and sunset. Is this the only cause? I
3 think that the increased loss of IO by reaction with HO₂ at noon could also play a
4 significant role.

5 We thank Dr. Sander for pointing to this reaction whose influence on the modeled IO top-hat
6 shape is now reflected in the manuscript:

7 *For the same heights as Fig. 10, the average diurnal variation of the main iodine species is*
8 *illustrated in Fig. 11. In the tropics, I and IO follow a diurnal concentration profile with a*
9 *characteristic top-hat shape due to the fast photochemical constants of the iodine system*
10 *which allows the rapid occurrence of the I-IO steady state. Note that the diurnal top-hat*
11 *shape of IO is also influenced by the daytime loss of IO by reaction with HO₂. IO is the*
12 *dominant daytime species below 5 km, while atomic iodine dominates above that height,*
13 *defining the diurnal temporal evolution of the tropical I ring. IO levels show a double peak at*
14 *dawn and dusk, which is most evident at lower altitudes. This is attributed to the reduced*
15 *photodissociation of the IO radical during sunrise and sunset, particularly at lower heights,*
16 *which favors the displacement of the steady state towards IO. During daylight hours, both I*
17 *and IO abundances remain almost constant with time, while at nighttime they are completely*
18 *converted to the reservoir species HOI and IONO₂.*

19
20 • Page 20008, lines 16-18: Is “Brasseur and Solomon (2006)” correct, or should it be
21 2005? Also, I’m not sure if this is the best reference for the family concept. As far as I
22 know, it was introduced by Crutzen & Schmailzl (Planet. Space Sci., 31, 1009-1032,
23 1983).

24 We appreciate the careful reading of Dr. Sander and his appropriate correction. The
25 publication year of the Brasseur and Solomon book has now been corrected. With respect to
26 introducing additional peer-review articles that used the ozone depleting family formalism,
27 we are confident that the citation to a widely extended text-book is the best option: different
28 papers had introduced slightly different definitions of each of the O_x families and loss
29 processes. To avoid confusions, in the original manuscript we explicitly introduced each of
30 the loss processes considered for each family in Table 3, which are the formulas that should
31 be used to reproduce our results. Thus, we think that the citation of additional articles with
32 different definitions might introduce confusion. We have modified the sentence as follows:

33 *...The O_x loss rates equations for the ozone-depleting families considered in this work are*
34 *presented in Table 5. The formalism used here is based on the catalytic cycles and chemical*
35 *families defined in Brasseur and Solomon (2005) with the inclusion of iodine-driven O_x*
36 *chemical losses (IO_x_{Loss})...*

37
38 • Page 20011, line 8: “annual average I/IO ratios of ~3 are modelled” Is this a noontime
39 average? Please explain how this value was calculated.

40 Yes, both I and IO radicals are photochemically driven, and the ratio I/IO favours the atomic
41 iodine levels during the day. We have corrected the text here and in the rest of the manuscript.
42 Additionally, we have added the following sentence defining the “noontime”, “nighttime” and
43 “24-hs” averages used for the Figures and Tables at the very beginning of Section 3, Results
44 and Discussions:

45 *...Besides the standard 24 hour averaged streaming, time dependent output for day and night*

1 *has been generated considering the noon (11:30–12:30) and midnight (23:30–00:30) local*
2 *time, respectively, for all latitudes and longitudes. Additionally, the Western Pacific (WP)*
3 *warm pool area was defined by the equator (0°) and the 20° N parallels, and the 120°E and*
4 *165°E meridians (see black rectangle in Fig. 7)...*

5

6 • **Page 20011, line 12: What is “Arrhenius behavior”? Wouldn’t it be sufficient to write**
7 **“temperature dependence” here?**

8 Certainly by stating “Arrhenius behavior” we are pointing out to the “temperature
9 dependence” of the $I + O_3 \rightarrow IO + O_2$ rate constant, which implicitly considers the Activation
10 Energy for the reaction. Indeed, JPL-2011 specifically state that:

11 *“The rate constant tabulation for second-order reactions (Table 1) is given in Arrhenius*
12 *form:*

13
$$k(T)=A \times \exp (-E/R / T)$$

14 *and contains the following information:”*

15 As other reactions for iodine shown in Table 1 include a pressure and temperature dependence
16 much more complex than the one given by the Arrhenius formulation (e.g., $IO + OIO$), we
17 believe it is convenient to keep the sentence as it was originally included in the conclusions.

18

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